Experimental Report

18/03/2015

Proposal:	**9-10-1374**	**Council:**	4/2014

Title: Deswelling of highly crosslinked polystyrene microgel colloids in colloid-polymer mixtures close to the glass transition lines

This proposal is a new proposal

Researh Area: Soft condensed matter

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Samples: polystyrene(PS)/toluene
fully deuterated PS/toluene

Instrument	Req. Days	All. Days	From	To
D11	2	2	21/11/2014	23/11/2014

Abstract:

We want to study the osmotic deswelling behaviour in concentrated polystyrene microgel dispersions close to glass transition lines on adding varying amounts of linear polystyrene. Such dispersions show an unusually strong shift of the glass transition to higher volume fractions on polymer addition which has been tentatively attributed to particle shrinkage leading to a reduction of the effective volume fraction. We want to verify this proposition and to assess in how far osmotic deswelling is responsible for the unusual behaviour. At the same time we intend to check whether a deswelling theory derived from macrogel data can be applied to microgels as well. This requires the determination of the particle form factors of the microgels in concentrated microgel-polymer dispersions which is only possible by neutron scattering with contrast variation, i.e. on host-tracer mixtures in toluene/toluene-D8-mixtures. To achieve this required Q-range and resolution use of D11 is requested.

Deswelling of highly crosslinked polystyrene microgel colloids in colloid-polymer mixtures close to the glass-transition lines

Colloidal systems of sterically stabilized PMMA particles or crosslinked polystyrene (PS) microgel particles serve as model systems for hard spheres. Due to their properties, these particles are suitable experimental systems for investigations of the dynamics predicted by mode-coupling-theory (MCT). For instance, they can be easily studied by dynamic light scattering (DLS). One of the most prominent effects predicted by MCT is the so-called re-entrant melting effect [1]. On introducing a short-ranged attractive force by addition of free, i.e. non-adsorbing, polymer chains the glass transition line first shifts to higher volume fractions φ, then bends over and recedes again to lower φ, thus creating a fluid pocket. It separates two types of glassy states – the repulsive glass at low polymer concentration c_P and the attractive glass at high c_P. In studies of binary mixtures of 1:50 crosslinked PS-microgels with free PS-polymer the existence of such a re-entry effect was verified. Fluid states up to volume fractions of $\varphi = 0.69$ [2] or even up to $\varphi = 0.715$ [3], depending on the size ratio $\delta = R_{g,polymer}/R_{colloid}$, were observed as shown in the inset of Fig.1. However, the extension of the fluid pocket in the PS-microgel mixtures is significantly higher than predicted by theory [1] and found for PMMA colloids [4]. One possible explanation is osmotic deswelling of the microgel particles as they are swollen in a good solvent by a factor of 5-6 in volume. To describe the extent of osmotic deswelling we followed the Bastide theory [5] for PS macrogels on addition of linear polystyrene. A predicted osmotic deswelling of 6 % would reduce the observed maximum fluid φ to 0.66 and 0.673 for $\delta = 0.078$ and 0.06, respectively.

However, it remains currently uncertain if a theory for deswelling of macrogels is applicable to microgel colloids as well. For this reason we studied the deswelling of our PS microgels in highly concentrated mixtures with free PS using SANS with contrast variation. For this purpose we investigated two host tracer mixtures. The first was composed of a fully deuterated 1:50 crosslinked PS-tracer ($R_{h,DLS} = 127$ nm) in a host of protonated 1:50 crosslinked PS-microgels ($R_{h,DLS} = 123$ nm) and free PS with $\delta = 0.06$. The second system consisted of a host composed of a binary mixture of two 1:50 crosslinked PS-microgels (radius $R_{h,DLS} = 123$ nm and 150 nm, size ratio $\Gamma = 0.82$) and free PS with $\delta = 0.03$ using the same tracer. The studied samples correspond to two equivalent state points in the phase diagram (cf. solid circles in the inset of Fig.1) using rescaled units. The tracer volume fraction was $\varphi = 0.03$ in all samples. For the second system a strong osmotic deswelling effect was anticipated. In a previous DLS study [6] on an analogous system no attractive glass transition following the melting of the repulsive glass was observed on addition of free polymer. This has been attributed to significant osmotic deswelling. To determine the particle form factors P(q) of the tracer in the different samples we used as solvents toluene/toluene-d8 mixtures with a deuterated molar fraction x_D = 0.11/0.12. These were observed to provide minimal average contrast of the respective host systems in a test experiment (TEST-2369).

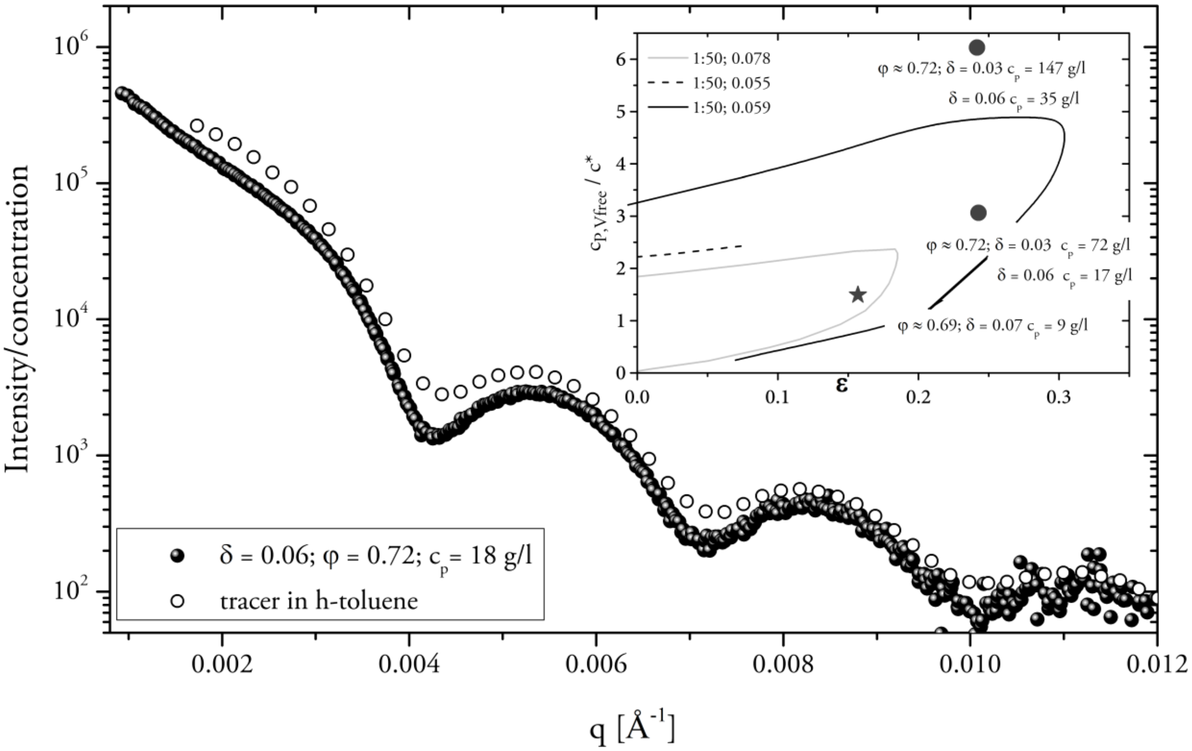

Fig.1 Scattering intensities of a dilute solution of fully deuterated PS-tracer microgel particles in toluene and of the same tracer in a concentrated PS-microgel-free PS-polymer solution with φ = 0.72, c_P = 17 g/l and a polymer to colloid size ratio δ = 0.06. The measurement of the concentrated sample was performed at minimum average contrast of the host in a mixture of toluene-d8 and toluene. The inset shows the phase diagrams of microgel-polymer mixtures with two different size ratios δ = 0.078 and 0.059 as indicated. Lines encircle fluid states. Polymer concentrations are given with respect to the free volume available in the colloid dispersion and are normalized to the overlap concentration c*; $\varepsilon = (\varphi-\varphi_g)/\varphi_g$, with φ_g = 0.595, and 0.577, respectively; solid circles indicate state points measured at D11 for δ= 0.06 and δ= 0.03. The tracer volume fraction was ~0.03 in all samples.

The expected shrinking in particle size is rather small. Thus, the required resolution around the first minimum of P(q) needs to be very high. Therefore we used an increased detector resolution (pixel density was increased from 128 x 128 pixels to 256 x 256) on D11 in combination with three different detector distances (28 m, 34 m and 39 m) at a wavelength of λ = 10 Å covering a q-range of $9\cdot10^{-4} \leq q$ / Å$^{-1} \leq$ 0.014. The improvement in resolution is demonstrated in the main Fig.1. The tracer particle form factor for the system with δ = 0.06 at the lower c_P is compared to that of the pure tracer in dilute solution, measured previously (TEST-2369) with standard resolution. With the q-resolution improved by a factor of ~8, a shift of the P(q) minimum by one data point now corresponds to a change in particle radius R

($q_{min} \cdot R = 4.49$) of ~0.5 nm as compared to 4 nm previously. Comparing the P(q) minima of both measurements – diluted solution of tracer and tracer in concentrated host – within the accuracy of the dilute tracer no shift in P(q) is visible. The same holds true for the higher polymer concentration of the system with $\delta = 0.06$. Its P(q) can be mapped onto that of the lower c_P (in terms of q·R) without need to adjust the tracer radius R (not shown in Fig.1 for clarity). In fact, fitting the measured intensities with a P(q) for polydisperse hard spheres returned R = 104±4 nm for the tracer in dilute solution and R = 105±1 nm for the tracer in the microgel-polymer mixtures with $\delta = 0.06$.

In contrast, the tracer P(q) in the system with smaller polymer to colloid size ratio $\delta = 0.03$ shows a clear shift of the minimum position with respect to the dilute tracer. This indicates an osmotic deswelling which increases with increasing c_P and results in a radius reduction of 5 nm and 9 nm, respectively, as shown in Fig.2. This finding is consistent with the disappearance of the attractive glass transition in an analogous system observed with DLS [6].

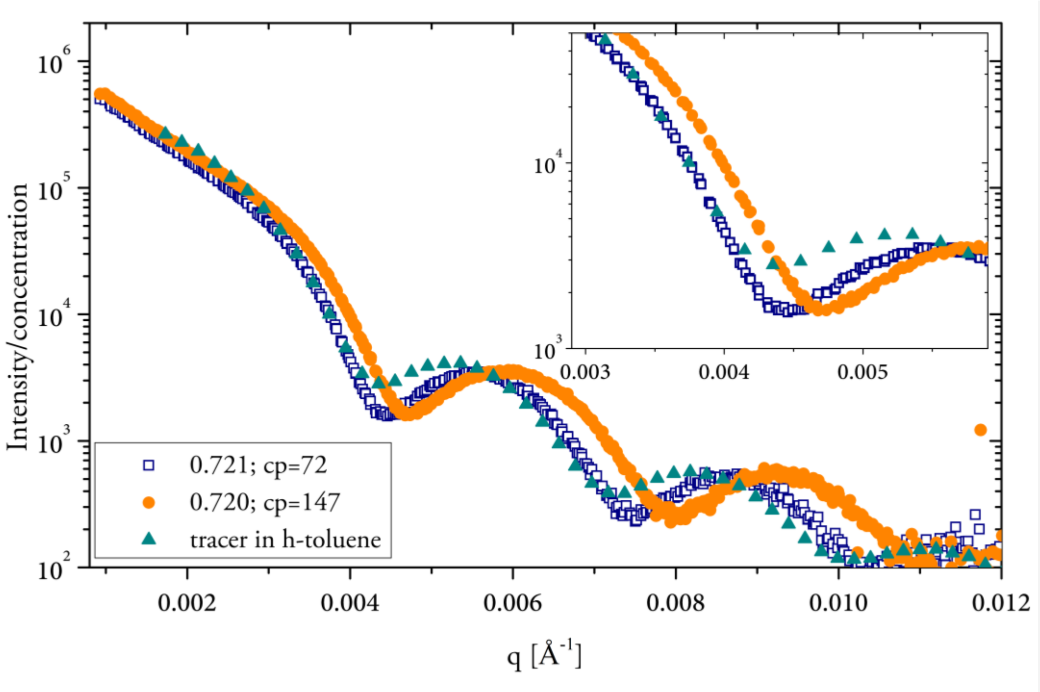

Fig.2 Scattering intensities of a dilute solution of fully deuterated PS tracer microgel particles in toluene and of the same tracer in concentrated PS microgel-free PS polymer solutions with a polymer to colloid size ratio $\delta = 0.03$, at the state points indicated in the inset of Fig.1. The measurements of the concentrated samples were performed at minimum average host contrast in a mixture of toluene-d8 and toluene.

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